# SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF HYBRID ION-EXCHANGERS

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**2002**

# Dedicated

*to*

*my*

# Family

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## CERTIFICATE

*This is to certify that the work presented in this dissertation entitled "Synthesis, Characterization and Applications of Hybrid Ion-Exchangers", has been carried out by Mrs. Vandana Jain. It is an original contribution of the candidate and is suitable for submission for the award of M.Phil. degree in Applied Chemistry.*

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Vandana Jain

*Vandana Jain*

# CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

## LIST OF PUBLICATIONS

1. Synthesis and Ion-Exchange Behaviour of Acrylamide Zirconium (IV) Phosphate: A Novel Crystalline and Hg(II) Selective Hybrid Inorganic Ion-Exchanger.

   ***Indian Journal of Chemical Technology***

   **(Communicated)**

2. Ion Exchange Kinetics of Alkaline Earth Metals on Acrylamide Zirconium(IV) Phosphate Cation Exchanger.

   ***Indian Journal of Chemistry***

   **(Communicated)**

# Chapter 1
# General Introduction

The systematic storage of knowledge gained as a result of conclusions drawn by experiments and practical applications is known as "Science". Chemistry is one of the basic Sciences which is further divided into analytical, organic, inorganic, physical and biochemistry. Analytical chemistry is the chemistry of the identification and separation of substances; the resolution of the substances into their components and their subsequent determination. Analytical chemistry is basically concerned with the determination of the chemical composition of matter. So far this was the main goal of analytical chemists. However, identification of a substance, the elucidation of its structure and quantitative analysis of its composition are the aspects covered by modern analytical chemistry. Chemical analysis is used as an intrinsic tool in geology, oceanography and air and water pollution. During the last few decades analytical chemistry has undergone such a revolution that it has come into the very foreground of advances in chemical sciences. Also, the scope and even the purpose, of analytical chemistry has grown amazingly in recent years. No other branch of Science finds so extensive an application as analytical chemistry purely for two reasons: one, it finds numerous applications in various disciplines of chemistry such as inorganic, organic, physical and biochemistry, and secondly, it finds large applications in other fields of sciences such as environmental sciences, agricultural science, biomedical and clinical chemistry, solid state research and electronics, oceanography, forensic sciences and space research.

The two important steps in analysis are "identification" and "estimation" of constituents of a compound. The identification step is called 'qualitative analysis' while estimation step is called 'quantitative analysis'. The methods involved in a chemical analysis may be 'instrumental' or 'non-instrumental'. The former methods involve the applications of the principles of Physics and Physical

Chemistry to the chemical analysis. They are usually much faster than the purely chemical procedures, and are applicable normally at concentration far too small to be amenable to determination by classical methods, and find wide application in industry. Despite the advantages possessed by the instrumental methods in many directions, their wide spread adoption has not rendered the classical methods obsolete. The following three reasons may be outlined in this connection:

1. The apparatus required for classical methods is cheap and readily available in all laboratories.

2. With most instrumental methods it is necessary to carry out a calibration operation using a sample of material of known composition as a reference. The exact analytical data for this standard must be established by the classical chemical methods.

3. It is often simpler to use a classical method rather than to go to the trouble of preparing requisite standards and carrying out the calibration of an instrument.

However, there is no fundamental difference between the two methods of analysis. For example, even a classical method like gravimetry involves the use of an instrument, such as, balance and discussion of non-instrumental methods is sometimes based on the principles of physical chemistry. The only difference between the two methods lies, therefore, in the degree of complexity of the instruments used. They must be regarded as supplementing each other.

Prior to a chemical analysis, separation of different constituents in a given sample is of primary concern for an analytical chemist. The methods generally used for separations include distillation, extraction, precipitation, crystallization, dialysis, diffusion etc. Out

of them chromatography, ion-exchange and electrophoresis are the modern and most versatile analytical techniques. According to Strain "chromatography is a separation method in which a mixture is applied as a narrow initial zone to a stationary, porous sorbent and the components are caused to undergo differential migration by the flow of the mobile phase, a liquid or a gas". Chromatography is relatively a new technique which was first invented by Russian botanist Michael Tswett, in 1906 in Warsaw for the separation and isolation of green and yellow chloroplast pigments by column adsorption chromatography. Kuhn and Lederer, in 1931, used this technique for the separation of carotene into the $\alpha$- and $\beta$- isomers. Since then, the technique has undergone tremendous modifications so that now-a-days various types of chromatography are in use to separate almost any given mixture, whether coloured or colourless, into its constituents and to test the purity of these constituents. The name chromatography (Greek chroma colour and graphy writing means colour writing). Essentially, the technique of chromatography is based on the difference in the rate at which the components of a mixture move through a porous medium (called stationary phase) under the influence of some solvent or gas (called moving phase).

Chromatography is useful for the comparison of substances, for providing clues as to the structures of organic substances, and for the detection of structural changes produced by the various chemical reagents or nuclear and biological processes. Combined with the conventional chemical and instrumental analytical methods, it serves to identify chemical species. Chromatographic methods have a nearly unlimited range of applicability. They can be used to separate smallest molecules ($H_2$, $D_2$) as well as the biggest (proteins, nucleic acids). Isotopes can be separated by gas chromatography combined with mass spectrometry. On the other hand, multigram quantities can be separated and isolated by

preparative column chromatographic methods. Chromatographic processes can be classified according to the type of equilibration process involved, which is governed by the type of stationary phase. Various bases of equilibration are adsorption, solubility, ion- exchange and pore penetration.

Various types of chromatographic techniques used in analytical chemistry are listed in the following table no. 1.1.

Ion- exchange chromatography uses an ion- exchange material as the stationary phase which is an insoluble material carrying the exchangeable cations (cation exchanger) or anions (anion exchanger). Certain materials are capable of both cation and anion exchange and are called 'amphoteric ion- exchangers'.

Ion-exchange is a process in which reversible stoichiometric interchange of ions of the same sign takes place between an electrolyte solution or molten salt and a solid phase as indicated below:

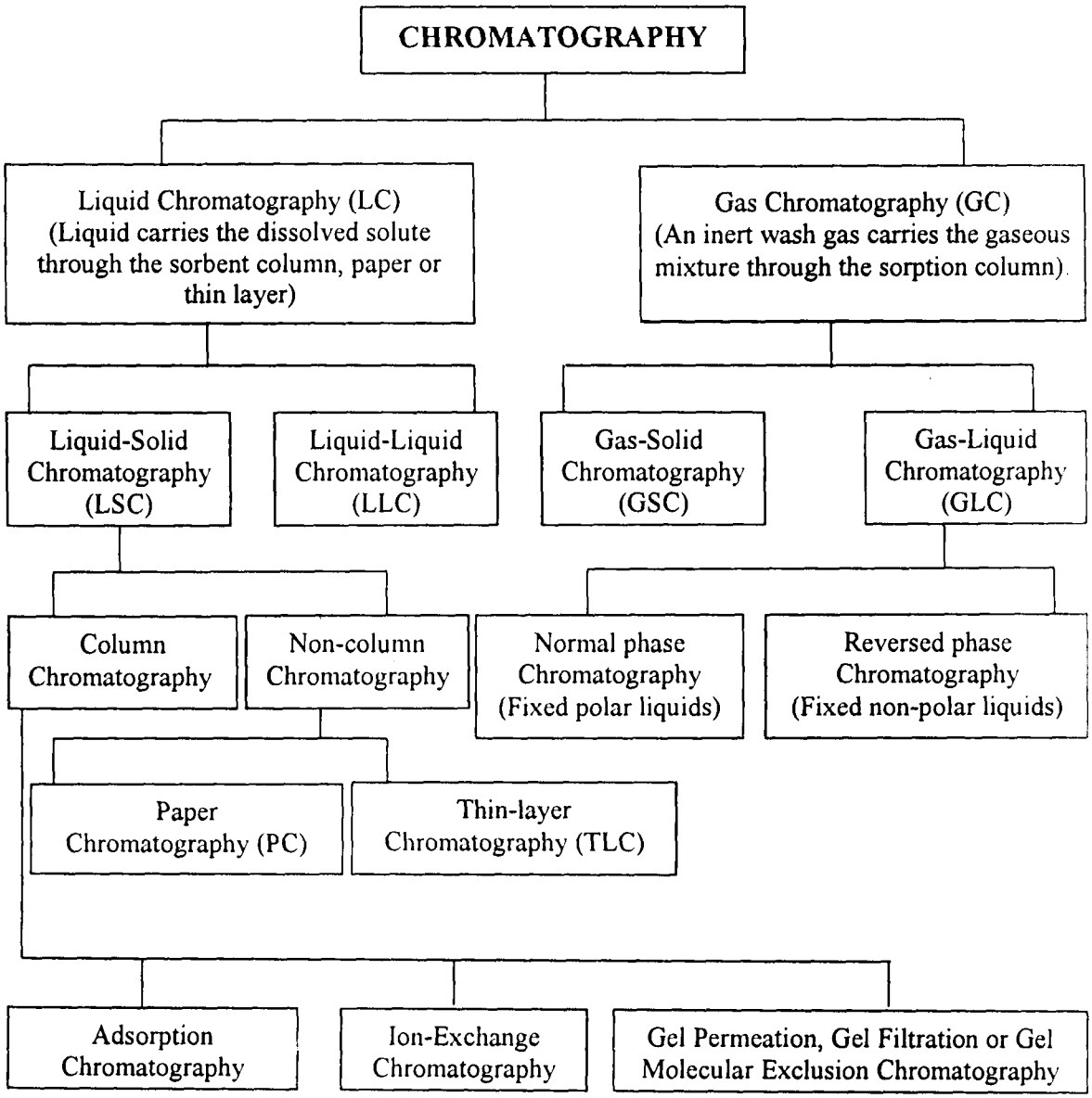
$$2\underline{NaX} + CaCl_2(aq) \rightleftharpoons \underline{CaX_2} + 2NaCl(aq) \qquad (1)$$

$$2\underline{XCl} + Na_2SO_4\,(aq) \rightleftharpoons \underline{X_2SO_4} + 2NaCl(aq) \qquad (2)$$

Equation (1) is a typical cation exchange reaction and equation (2) is a typical anion exchange reaction. In equations (1) and (2) 'X' represents a structural unit of the ion exchanger; 'aq.' indicates that the electrolyte is in aqueous solution and solid phases are underlined.

Many million years ago, ion- exchange phenomenon had occurred in various sections of the globe. For example, some ions like potassium and lithium ions of petalite of pegmatite veins had been replaced with rubidium and cesium ions of stepwisely coming fluid from the magma. This is nothing but ion-exchange phenomenon between minerals like petalite (solid phase) and fused

**Table 1.1** Various chromatographic techniques used in analytical chemistry



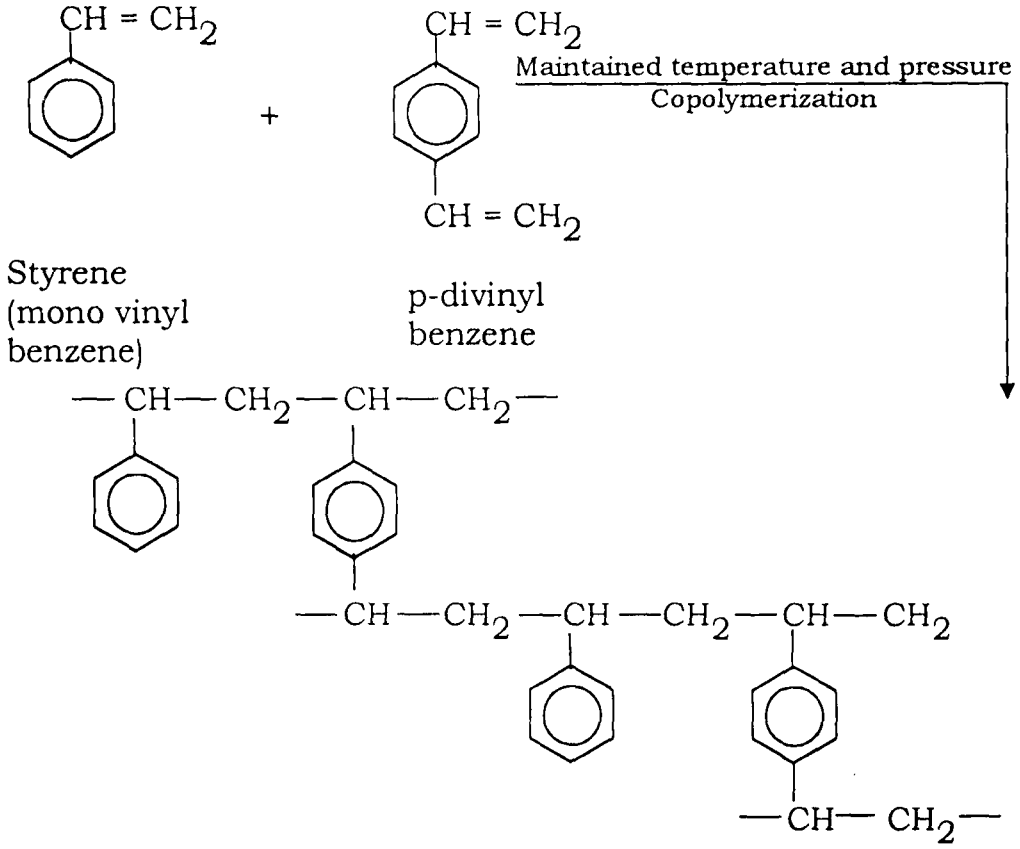
salt fluid (liquid phase) [1]. It is well known that ion-exchange has been playing very important role during the courses of weathering. Aqueous rocks, clay rocks, and soils are very effective ion-exchangers. Since life had been created in the sea, ion-exchange through bio-membranes between living organs and outside matters has been giving the essential motive forces to life and its evolution. In Egypt and Greece as well as in China, ancient people were clever enough to use some soil, sand, natural zeolites and plants as the tools for improving the quality of drinking waters, desalting or softening. They did not know anything about ion- exchange. Nevertheless, they had experiences enough to use them as water softener or desalter. The reference of ion-exchange can be found in the Holy Bible also, which establishes Moses' priority in this field. About a thousand years later, Aristotle [2] suggested filtration of sea water through a certain type of soil, which removes part of its salt content. After that, only scarce references are found until around 1850, Thompson [3] and Way [4,5] discovered base exchange in soils. Later on, Lemberg [6,7] and Wiegner [8] identified clays, glauconites, zeolites and humic acids responsible for the ion- exchange phenomenon in soils. Harm and Rumpler [9] synthesized the first aluminosilicate based ion-exchanger in 1903, while Folin and Bell [10] first applied a synthetic zeolite for the collection and separation of ammonia from urine. The industrial production and technical applications of ion-exchangers were however studied by Gans [11,12].

**Organic and Inorganic Ion-Exchangers:**

The ion-exchange materials may be organic or inorganic in nature. Organic ion-exchangers, commonly known as 'ion-exchange resins', are known for their uniformity, chemical stability and high mechanical strength, whereas inorganic ion-exchangers are important for their good stability towards temperature, oxidizing solutions and ionizing radiations.

Organic ion-exchange resins consist of an elastic three-dimensional network of hydro-carbon chains which carry fixed

ionic groups. The charge of the groups is balanced by mobile counter ions. The resins are cross-linked polyelectrolytes. They are insoluble, but can swell to a limited degree. The ion-exchange behaviour of the resins depends chiefly on the nature of the fixed ionic groups. Organic ion-exchangers may be natural or synthetic. Sulphonated coal is an example of natural organic ion-exchanger. Synthetic organic ion-exchange resins are superior to other materials because of their high chemical stability, high mechanical stability, high ion-exchange rates, high ion-exchange capacity and versatility. The most important synthetic organic resins are of polystyrene and divinyl benzene type. Copolymer product of styrene and divinyl benzene is responsible for cross-linking which can be shown as:



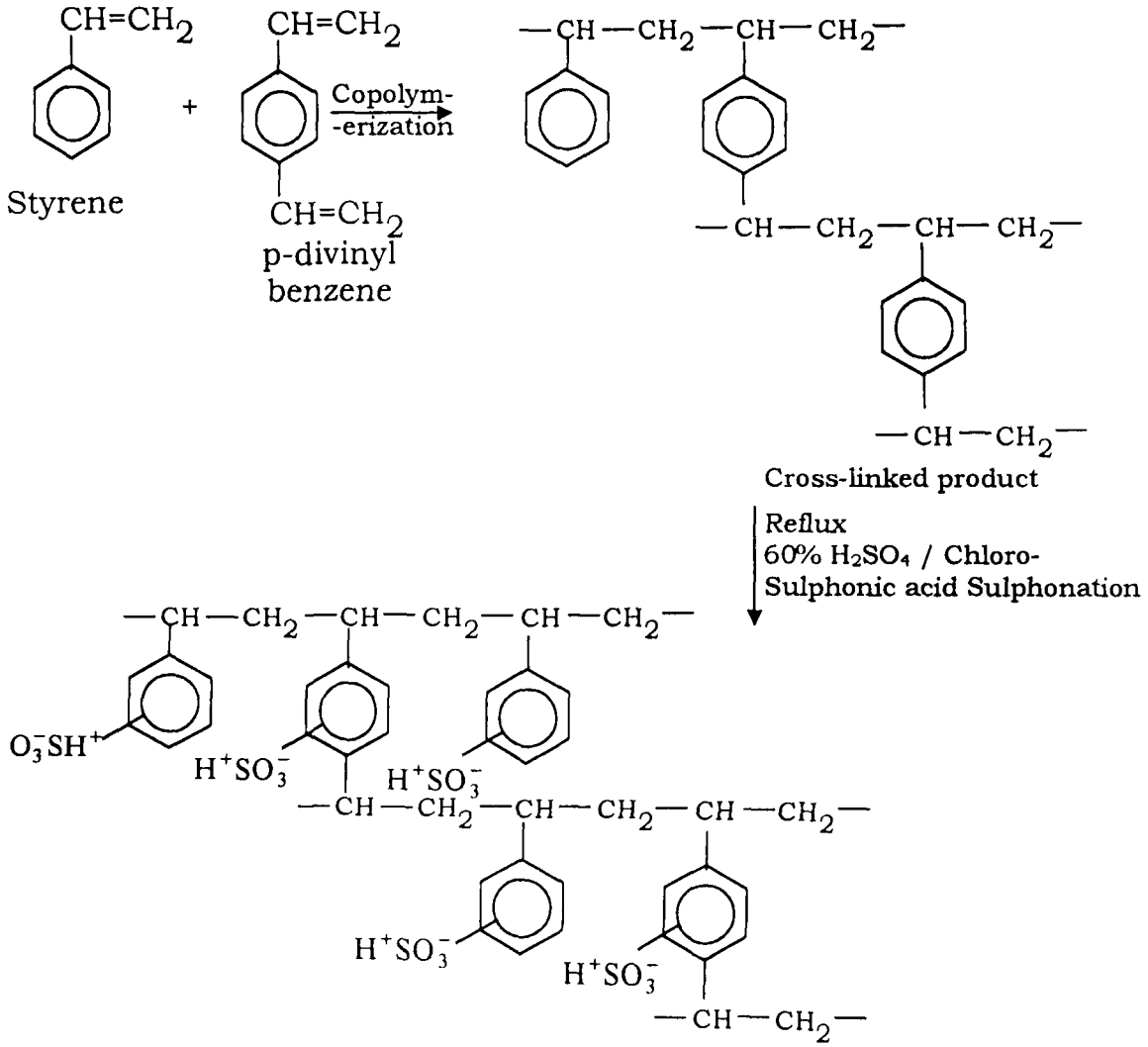

Organic ion-exchanges may be cation exchanger and anion exchanger. Cation exchangers are further divided into strong acid cation exchanger and weak acid cation exchanger; and anion exchangers are further divided into strong base anion exchange resins and weak base anion exchange resins.

## 1. Cation exchange resins:

Most of the earlier cation-exchange resins were condensation products of phenol derivatives and aldehydes. Sulfonic (strong-acid), carboxylic (weak-acid), or phosphonic acid groups (intermediate acidity) are usually introduced into the phenolic component. However, sulphonated aldehydes have also been used. The most important cation exchangers are sulfonation products of cross-linked polystyrene (strong acid), and cross-linked copolymers of acrylic or methacrylic acid (weak acid). Phosphonic acid groups have also been introduced into polystyrene.

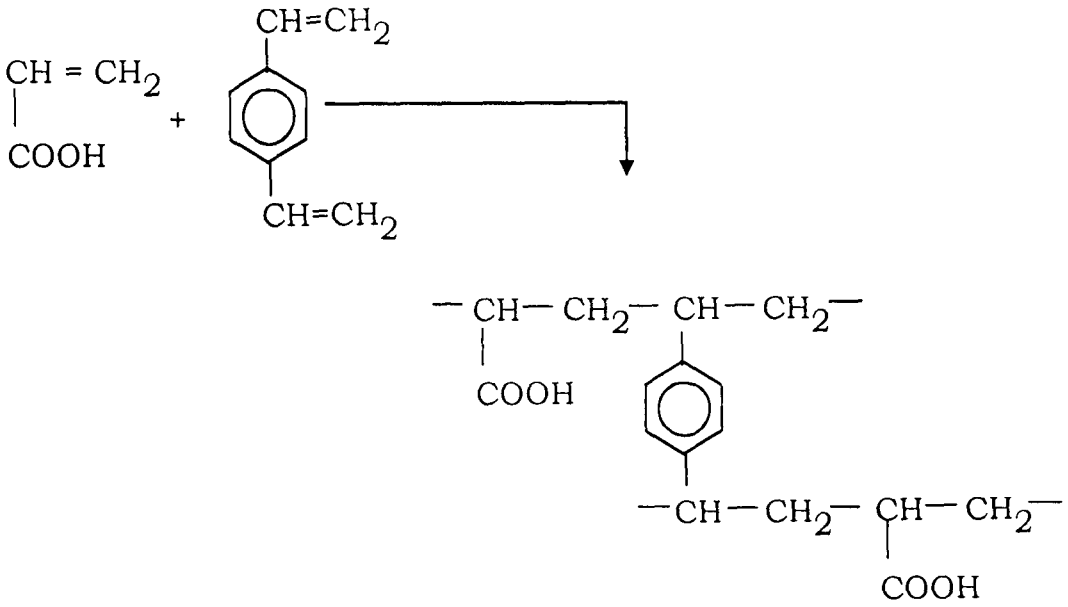
### (a) Strong acid cation exchange resins:

**Preparation:**



**(b) Weak acid cation exchange resins:**

**Preparation:**



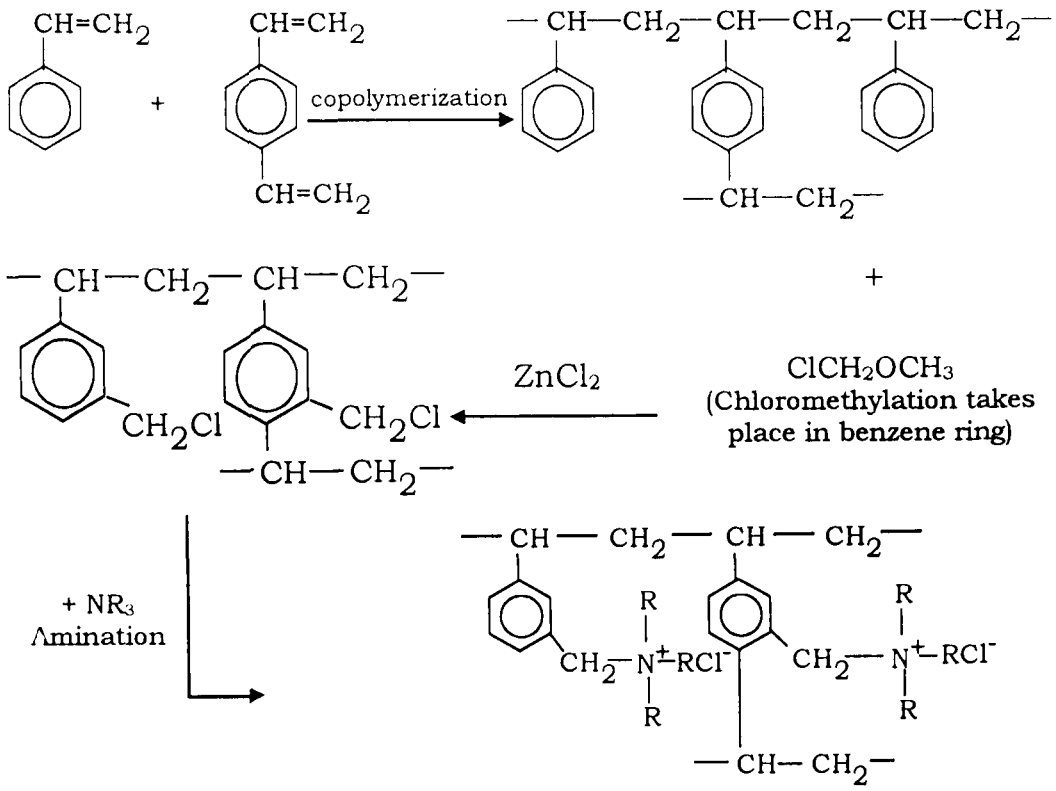
Examples of cation exchange resin are Amberlite IR-120, Dowex 50, Nalcite HCR, Permutit Q, Duolite C-20 and C-25 and Lewatit S-100.

## 2. Anion exchange resins:

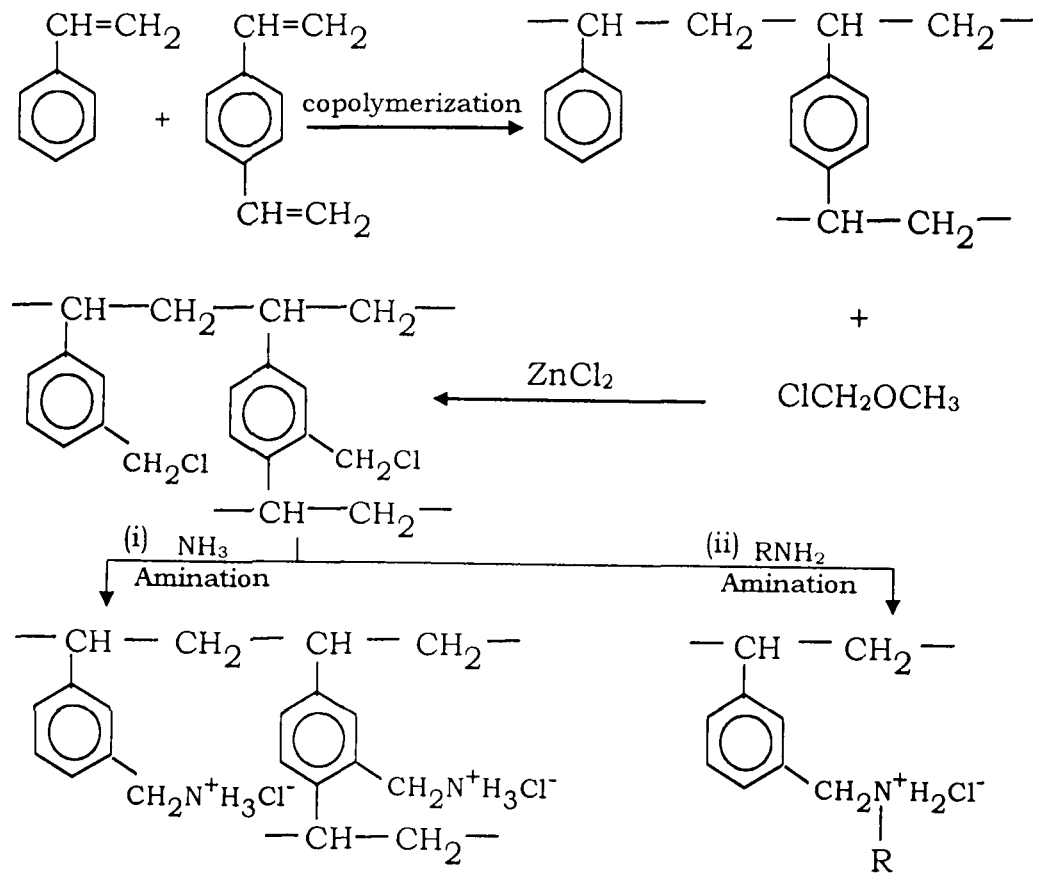
Most of the earlier anion exchange resins were condensation products of aromatic or aliphatic amines and aldehydes, dihaloparaffins, or haloepoxides (epichlorohydrin). Most of these resins contain primary, secondary and tertiary amino groups and are weak- base and polyfunctional materials. The most important anion exchangers are cross- linked polystyrenes into which strong- or weak base groups have been introduced by chloromethylation and subsequent amination. Reaction with tertiary alkyl amines gives strong- base quaternary ammonium groups, and reaction with primary or secondary alkyl amines or ammonia gives weak-base amino groups.

## (a) Strong base anion exchange resins:

### Preparation:




## (b) Weak base anion exchange resins:



Examples of anion exchange resin are Amberlite IR- 45, Dowex 3, Nalcite WBR, Duolite A-14.

Although organic resins have wide application in analytical chemistry because of their high stability in wide range of pH, reproducibility in results, the main drawback has been their unstability under conditions of high radiation at elevated temperature. This was the reason why an interest in the synthesis and ion-exchange properties of inorganic ion-exchange materials was developed. Inorganic ion- exchangers are thus having good applications in the treatment of industrial and radio- active wastes and processing of radio- isotopes in nuclear technology. They also have applications in determination and detection of metal ions in pharmaceutical and biological products, analysis of alloys and rocks and as ion- selective electrodes and packing materials in ion-chromatography. Thus, they are also important in environmental analysis [13]. In technical practice column operation (percolation through a filter bed) was used at an early stage. This principle was introduced into analytical chemistry by Whitehorn [14], who used a synthetic zeolite as a reagent for amines. In 1927 Bahrdt [15] published a method for the rapid esrimation of sulphate in natural waters. Certain organic materials with ion-exchanging properties have been known for a long time. Among cation exchangers the foremost, cellulose, has been thoroughly studied. Kullgren [16] showed that unbleached sulfite pulp contained sulfonic acid acid groups of a strongly acid character. Sulfonic acid groups are firmly attached to the pulp, whereas the corresponding hydrogen ions are dissociated and may be exchanged for other ions. Organic ion-exchangers for technical use were described during the 1930's in many patents. Cation exchangers produced by the sulfonaton of coal found technical applications, and cation exchange resins were later obtained. The basic patent concerning these resins was taken out in 1935 by Adams and Holmes [17]. These workers are also the

originators of anion exchange resins, which are to be recognized as insoluble resins containing basic groups, for example, amino groups having the ability to form salts with common acids.

Synthetic inorganic ion- exchangers have been studied quite extensively. Kraus [18, 19], Amphlett [20, 21], Clearfield [22, 23], Alberti [24], Inoue [25] and Abe [26] are the pioneers in this field. In India, Qureshi [27-30] and coworkers started this work in early sixties. Later on De *et al.* [31-35], Tandon *et al.* [36-40], Rawat *et al.* [41] Varshney *et al.* [42-46] and others took up the researches in this highly promising area and found some encouraging and useful results particularly in the environmental analysis. Important advances in the field of synthetic inorganic ion-exchangers have been reviewed by a number of workers at the various stages like Fuller [47], Vesely and Pekarek [48], Clearfield [49-50], Qureshi and Varshney [51], Varshney and Mohammad [52] and others.

Clearfield and Stynes [53] demonstrated that zirconium phosphate could be crystallized. Subsequently, single crystals were grown and the structure of the α-polymorph of zirconium phosphate determined [54-56]. This permitted the observed ion-exchange behaviour to be explained on the basis of structural concepts. Very recently the crystal structures of the $Na^+$ and $K^+$ forms of α-zirconium phosphate have been solved and a mechanism for the exchange process proposed [57-59].

Lately much interest has been developed in the synthesis and characterization of pillared inorganic materials and organic-inorganic hybrid structures arising from alteration of layered exchangers. The main advantage of a pillared structure is that it allows ready access of large ions and complexes to the interior due to the increase in the interlayer distances and pore sizes. This is very much useful in radio-active waste cleanup. A large number of radioactive species can be exchanged into the pillared materials

and then permanently sealed by heating to high temperatures. Also the size of the pores can be controlled by altering the charge on the pillaring cations. Exchange of cations into pillared materials can change their catalytic properties.

**Hybrid Ion-Exchangers:**

Hybrid ion-exchangers are prepared as a new class of ion-exchangers by incorporation of a polymeric material into inorganic ion-exchange materials. They can be prepared as three dimensional porous materials in which layers are crosslinked or as layerd compounds containing sulfonic acid, carboxylic acid or amino groups., The various types of hybrid ion-exchangers which were prepared earlier are listed in Table 1.2. The purpose of this study is, therefore, to prepare a hybrid ion-exchanger which possesses the properties of both organic and inorganic ion-exchangers and prove to be highly stable and possesses reproducible properties. Also, it should illustrate some real analytical applications.

**Table 1.2** List of some hybrid ion-exchangers prepared so far with their references and selectivity.

| S.No. | Material | Selectivity | Reference |
|---|---|---|---|
| 1. | Pyridinium-tungstoarsenate | Rb(I), Cs(I) | [60] |
| 2. | Zirconium(IV) sulphosalicylophosphate | -- | [61,62] |
| 3. | Styrene supported Zirconium-phosphate | -- | [63] |
| 4. | Acrylonitrile based cerium(IV) phosphate | Hg(II) | [64] |
| 5. | Polyanilinc Sn(IV) aresenophosphate | Pb(II) | [65] |
| 6. | Polyacrylonitrile thorium(IV) phosphate | Pb(II) | [66] |
| 7. | Polystyrene Thorium(IV)phosphate | Cd(II) | [67] |

Efendiev, Sultanov and coworkers [68] synthesized complex-forming ion-exchangers having increased ion-exchange capacity with respect to transition metals by reacting polyethyleneamine with a transition metal salt solution, followed by crosslinking with N, N-methylenediacrylamide and removal of the metal from the crosslinked copolymer. Makarova, Ivanova and coworkers [69] suggested a method for the improvement of the production of ion-exchange polyacrylonitrile fibres by treating freshly-spun roving with an alkaline agent with subsequent compression, washing and drying. $Zr(SeO_3)_2$ was prepared and characterized as an ion-exchanger [70]. Its optimal capacity and stability were demonstrated over results at other stoichiometries. The capacity of the exchanger for alkali metal and alkaline earth metals was measured. Its selectivity was studied through quantitative separation of Zn-Pb, Cu-Pb and Hg-Pb and by calculation of partition coefficients of Mg, Ca, Sn, Th, Pb, Bi and 6 transition metals. Tsuji, Sugita and Abe [71] prepared a new crystalline hydrous lithium titanate $(Li_{1.81},H_{0.19})Ti_2O_5.2.H_2O$, hydrothermally at 190° by a reaction of hydrous titanium di-oxide with LiOH-solution. Harkins and Schweitzer [72] prepared site selective ion-exchange resins by copolymerization of styrenic monomers with metal ion complex compounds bearing polymerizable ligands. Varshney and Khan [73] suggested the method for the synthesis, characterization and analytical applications, exchange kinetics and thermodynamics of amorphous inorganic ion-exchangers such as hydrous oxides, polybasic acid salts, insoluble metal ferrocyanides, hetropolyacid salts and stannic arsenate. Gong, Kuang and coworkers [74] suggested the method for the synthesis of phosphate ion-exchangers and their applications in the catalysis of petrochemical industry, separation of radioactive isotopes from products of nuclear fission, metal recovery from sea-water, softening of industrial waters, and treatment of waste waters.

Sun and coworkers [75] studied that Titanium-phosphate-ammonium phosphomolybdate can be used as esterification catalyst in the preparation of aspirin. Yu, Sun and coworkers [76] proposed the method for the synthesis and XPS study of titanium phosphate-ammonium tungstophosphate. A new complex inorganic ion-exchanger, zirconium-stibopyrophosphate-ammonium molybd--ophosphate ($ZrSbP_2$-AMP) [77] was synthesized. The complex was investigated by thermal analysis, electron microscopy, IR spectrometry and chemical analysis, chemical composition and some related properties of the ion-exchanger were reported. The ion-exchange behaviour of the ion-exchanger were also studied in detail on $Na^+$, $K^+$, $Cs^+$, $Cu^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Sr^{2+}$ and $Al^{3+}$. The complex inorganic ion-exchanger showed high ion-exchange capacity. Yu and Sun [78] also proposed a method for the synthesis and characterization of inorganic ion-exchanger titanium phosphate-ammonium tungstophosphate. Sun and coworkers [79] studied the new complex inorganic ion-exchanger titanium-pyrophosphate-ammonium molybdophosphate.

The exchangers are obtained by firing composite gel prepared from a mixture of organic metal compound containing solution and ion-exchange inorganic powder by sol-gel process [80]. The method for the preparation of $CaSiO_3$ containing ion-exchangers by hydrothermal treatment of burned waste paper sludges was suggested by Nagasawa, Yoshimura and coworkers [81].

Boichinova, Nikolaeva and coworkers [82] determined the optional conditions for synthesis of ion-exchanger TFT's from zirconium(IV) chloride oxide. Boichinova, Safina and coworkers [83] studied the kinetics of sorption of copper(II), cobalt(II) and nickel(II) ions on zirconium aluminopyrophosphate, organic ampholytes and AN-31 anion exchanger. The mechanism and selectivity of ion-sorption by zirconium-based inorganic ion-exchangers was studied by Boichinova and coworkers [84]. Bondarenko and Boichinova

[85] studied the effect of synthesis conditions on the properties of the inorganic electron ion-exchanger zirconium silicomolybdate.

Oliveira and coworkers [86] suggested the methods for the synthesis, characterization of amorphous titanium(IV) phosphate exchanger through elemental, analytical, IR and TGA techniques. Singh and Lal [87] prepared and studied the properties of Iron(III) tungstophosphate by IR spectrophotometry, thermogravimetric analysis and pH-titration. Zirconium phosphate or phosphonates, whose compounds have the general formula $Zr(O_3PR)_2$, can be obtained in crystalline forms with various layered structures [88]. The preparation and characterization of two-dimensional zirconium phosphonate derivatives were investigated. Two composite zirconium phosphonates in a single-crystal phase were also investigated and characterized by X-ray diffraction and $^{13}C$ and $^{31}P$-magic-angle spinning NMR. These compounds are lamellar structures comprising zirconium phosphates or organophosphonates. Each layer consist of planes of zirconium-bridged through phosphonate groups that alternate above and below the zirconium atom planes, oriented away from the basal surfaces in a bilayered fashion in the interlayer region. The catalytic performance over zirconium phosphonates was evaluated by esterification of acetic acid. When the composite zirconium phosphonate includes an acidic function and a hydrophobic function in the single-crystal phase, the catalytic activity was higher than that of single-acidic-function zirconium phosphonate. The composite materials become accessible to any reactant molecule, and their hydrophobicity improves.

Oosumi, Sugiura and coworkers [89] suggested the method for the manufacture of crystalline zirconium phosphate, Chen, Ye, and coworkers [90] prepared magnetic polystyrene resins by suspension polymerization with the addition of $\gamma$-$Fe_2O_3$ into the styrene divinylbenzene prepolymer. The topotactic exchange reactions of $\gamma$-

zirconium phosphate and γ-zirconium-phosphate methyl phosphonate with phosphonic acids derived from azacrown ethers of different sizes was examined. Prior intercalation of hexylamine was necessary in most cases to attain the maximum exchange level predicted by molecular modeling. Materials with imbricated or non-imbricated layers were obtained depending on crown size and exchange level. Exchange of methyl phosphonates in γ-zirconium phosphate/methyl phosphonate was only observed when hexylamine had previously been intercalated. The exchange with the biphosphonic acid derived from 1,10-diaza-[18]-crown-6 gave a material with an interlayer distance compatible with pillaring of the γ-phase. The materials obtained from the exchange reactions of γ-zirconium-phosphate with phosphonic acids derived from [12] crown-4-and [18] crown-6 showed thermodynamic selectivities towards $Na^+$ and $K^+$ respectively, that were much higher than those observed for the simple crowns in solution. The inorganic molecular framework enhances molecular recognition by minimization of solvation effects [91]. Nabi, Usmani and Rahman [92] synthesized samples of Zr(IV) iodophosphate under varying conditions at pH-1. The most chemically and thermally stable sample is prepared by adding a mixture of aqueous solutions of 0.1 M potassium iodate and 0.1 M Zr oxychloride. Its i.e.c. for Na+ is 1.78 meq/dry gm exchanger. The material was characterized from chemical composition, FTIR, TGA and DTA. The effect of heating on the exchanger at different temperatures on the exchange capacity also was studied. The sorption behaviour of important metal ions in HCl-DMSO system was studied. A number of analytically important metal ion separations was achieved. The practical utility of these separations was demonstrated in the analysis of antacids drug samples. Wakamatsu, Sakurai and coworkers [93] suggested a method for the manufacture of ion-exchangers and removal of multicharged anions with the ion-exchangers. Samples of zirconium phosphate have been synthesized by zirconium building up on colloid particles of aluminium hydroxide followed by $H_3PO_4$

or $Na_3PO_4$ treatment. Adsorption structure properties of these samples have been studied and the samples containing built up zirconium phosphate have been shown to possess a good developed pore structure and specific surface. It has been established that structure parameters of zirconium phosphate are changed with carrier structure changing due to duration of hydroxide precipitation. Such pore phosphates can be used not only as ion-exchangers but as catalysts of oxidizing dehydration and a number of other catalytic processes as well [94].

Layered sodium zirconium arsenate $Zr_2O_3(NaAsO_4).3H_2O$ was prepared by the reaction between $Zr(OPr)_4$ and sodium arsenate in alkaline media (pH > 12) under mild hydrothermal conditions (180-200°). Two hydrogen forms of the zirconium arsenate ($\Psi$-ZrAs)$Zr_2O_3(HAsO_4).3H_2O$ and $Zr_2O_3(HAsO_4).H_2O$, were prepared by acid treatment of the sodium form. The intercalation of n-alkylamines into the $\Psi$-ZrAs from the gas phase was studied. The synthesized materials were characterized by elemental analysis, TGA, IR spectroscopy and powder X-ray diffraction. The Zirconium arsenate is isostructural to $\Psi$-$Zr_2O_3(HPO_4).nH_2O$(n=0.5,1.5). The new compounds exhibit high hydrolytic stability in alkaline media. The ion-exchange behaviour of the $\Psi$-$Zr_2O_3(HAsO_4).3H_2O$ towards alkali, alkaline earth, and some di and trivalent metal cations in different solutions was studied over a wide pH-range (2-14) by the batch technique [95]. Anion exchange properties were studied for Ti and Zr phosphates. The effects of exchanger chemical state, extent of aging, nature of the anion, and medium acidity on the effectiveness of anion sorption were studied. Comparison of data for $PO_4^{3-}$, $SO_4^{2-}$ and $Cr_2O_7^{2-}$ and also $Co^{2+}$ sorption show that exchangers with low phosphorus content have amphoteric properties, 2-4 mg/equiv./g anion exchange capacity and 3-5 mg/equiv./g cation exchange capacity [96]. Grafova, Bortun and coworkers [97] studied the non-traditional use of new inorganic ion-exchangers as functionally graded sorbents.

Pandit and Chudasama [98] suggested a method for the synthesis, characterization and application of a derivatized acid salts of tetravalent metal: o-chrolophenol anchored onto Zr-tungstate. Beena and Chudasama [99] proposed a comparative study of the Broensted acidity of zirconium phosphate and Zr-phenyl phosphonate.

Liang [100] prepared an amphoteric ion-exchange resin which can be used for decolorizing and iron removing purposes and is a condensation polymerization product of m-phenylenediamine, resorcinol and formaldehyde. A porous resin loaded with monoclinic or cubic hydrous zirconium oxide was prepared by incorporation of $ZrOCl_2.8H_2O$ into porous spherical polymer beads followed by hydrolysis and hydrothermal treatment of the zirconium salt. Hydrous zirconium oxide appeared to deposit inside the pores with relatively large diameter. The adsorption capacity and distribution coefficients for As(III) and As(V) (.3Uwere determined by batch procedures. The hydrous zirconium oxide loaded resin (Zr-resin) showed a strong adsorption for As(V) at slightly acidic to neutral pH-region while As(III) was favorably adsorbed at pH-around 9 to 10. The removal of low concentrations of arsenic from the model effluents to meet the demand of Japanese industrial effluent standard (0.1 ppm) was successfully achieved by the column operation packed with the Zr-resin. The Zr-resin was regenerated by treatment of the column with 1M sodium hydroxide followed by conditioning with 0.2M acetate buffer solution. The amount of zirconium leached out during the adsorption and regeneration cycles was negligibly small and the column can be used repeatedly [101].

Qureshi, Asif and coworkers [102] suggested a method for the synthesis and characterization of Zr(IV) 4-amino, 3-hydroxy naphthalene sulfonate ion-exchanger: quantitative separation of mercury from numerous metal ions. Qureshi and coworkers [103]

also proposed a method for surface interaction of ethanolamine with hydrous Zr(IV) oxide gel: characterization and separation of some anionic species by column chromatography. A new ion-exchanger phase, saw dust based zirconium(IV) tungstophosphate was synthesized and characterized with the help of ion-exchange, elemental analysis, IR and TGA studies. Its chemical stability was checked both in acidic and alkaline media. Kinetics of exchange of alkaline earth metal ions on this material was also studied to understand its exchange behaviour [104]. Kubica and coworkers [105]. Kubica and coworkers [105] proposed a method for the sorption of Hf, Zr, and Nb on organic and inorganic ion-exchangers from mineral acid solutions. Sarkar and Basu [106] suggested the method for the preparation of zirconium tungstate and liquid chromatographic separation of metal ions. Abe and coworkers [107] proposed a method for the comparative study of lithium recovery from sea water with various inorganic ion-exchangers. Mc Garvey and coworkers [108] suggested a method for removal of toxic heavy metals from industrial waste water by selective ion-exchange resins. Mc Garvey and coworkers [109] described the production of water for the semi-conductor industry through ion-exchange processes. Lobo and Turel [110] studied the adsorption and radiochemical separation of Zr(IV) from other elements, employing Zr-phosphate ion-exchanger. They also developed a method for adsorption and radiochemical separation of cesium(I) from other metal ions by absorbing it on Zr-phosphate ion-exchanger [111]. Chekhomova and coworkers [112] proposed a method for the extraction and separation of Samarium and neodymium on Zr-phosphate, serving as an inorganic ion-exchanger.

Shakshooki and coworkers [113] proposed a method for selectivity of mixed zirconium-titanium phosphates toward transition metals. Shakshooki and Szirtes [114] studied the effect of gamma-radiation on amorphous mixed Zr-titanium phosphates.

Szirtes and coworkers [115] also studied the thermal behaviour of acidic salts of mixed tetravalent metals. III. Influence of gamma-radiation on the thermal decomposition of mixed zirconium-titanium phosphates. Aboul-Magd and coworkers [116] investigated the studies on the esterification of 1-propanol and 1-butanol with some organic acids using inorganic ion-exchange resin (zirconium-tungstate) as a catalyst. Hao and coworkers [117] studied the conductivity of a complex inorganic ion-exchanger-α-Zr-phosphate mixed with silica. Ito and coworkers [118] proposed crystalline Zr-phosphates with zeolite like porous structures for ion-exchangers and other applications. Singh and Archana [119] proposed electrochemical studies on Zr-phosphate-kynar composite ion-exchange membrane system. Kociolek-Balawejdar [120] synthesized macro molecular disinfectants as a product of chemically modified ion-exchange resin which are to be used under specific conditions for potable water disinfection.

Combustion by product fly ash was converted into zeolites which then can be used as ion-exchangers for waste treatment applications. The conversion process not only alleviates the disposal problem of large amounts of fly ash, but also turns fly ash into a useful material. Depending on the treatment temperature and chemical composition, zeolite A and faujasite were successfully synthesized. The ion-exchange capacity of the treated fly ash was examined. The results show that the ion-exchange capacities of the treated fly ash in the forms of zeolite A and faujasite, respectively, for $Cs^+$ ions relative to those of the commercial zeolite A and faujasite are 19% for zeolite A phase and 39% for faujasite phase [121].

Out of a large number of the insoluble acid salts of polyvalent metals. Zirconium phosphate is probably the most exhaustively studied material, both in the amorphous and crystalline forms [122-126]. In electrodialysis applications, membrane of zirconium

phosphate withstands conditions of temperature and pressure which causes deterioration to the organic resins. It is attractive for desalination applications [127-128] and for use in hydrogen-oxygen fuel cells [129-131]. Papers impregnated with zirconium phosphate have been, successfully, used for the rapid chromatographic separations of bivalent and tetravalent metal ions, and of amino acids and alkaloids [132]. The high selectivity of this salt for $NH_4^+$ ions in presence of sodium ions has prompted the investigation of its use in artificial kidneys [133]. A systematic investigation in this field has resulted several new crystalline ion-exchangers other than zirconium phosphate. Cerium(IV) phosphate [134] and thorium(IV) phosphate [135] have a distinction of being the only insoluble acid salts having a fibrous structure. Fibrous inorganic ion-exchangers are very interesting because they can be used in the preparation of inorganic ion-exchange papers, or thin layers suitable for chromatographic separations. These materials have also been employed for preparing inorganic ion-exchange membranes which are interesting both fundamentally and practically. Due to their high selectivity and stability these membranes have been used as selective electrodes where organic membranes fail. They can also be employed in fuel cells at high temperature. Ion exchange fibres, new materials, can be used in the form of various textile goods, such as cloth, conveyer belts, non-woven materials, staple, nets, etc. Ion exchange fibres can be used in the same chemical processes as conventional ion-exchangers since their chemical structure is similar. At the same time an unusual physical form opens new technological possibilities. Moreover, metal recovery from ores is not the only field for the use of ion-exchange fibres in hydrometallurgy, they can be used in wastewater treatment, metal recovery from natural reservoirs and air purification from impurities of acidic or basic nature. The textile form of ion-exchangers allows easily controlled movement of them in aqueous or gaseous media. Appropriate forms of ion-exchangers can be conveyer belts, nets, floating mats or those fixed in the water

streams, etc. In all these cases there is no need in water pumping through the layer of ion-exchangers which is most important in treatment of large volumes of water in open reservoirs. Continuous sorption or desorption processes can be easily organized for the moving ion-exchange belts. Non-woven mats are convenient for gaseous processes where low resistance for airflows is basic requirement. An important advantage of fibrous ion-exchangers is their extremely high osmotic stability which allows using them in conditions of multiple wetting and drying occurring at cyclic sorption or regeneration processes in air purification. Ion-exchange fibrous materials open new technological possibilities for metal ions recovery, purification of wastewater and treatment of water in natural reservoirs. Ion-exchange fibres have especially great advantage in air purification from acidic and basic impurities. FIBAN® ion-exchange fibres offer a collection of characteristics suitable for their practical application: high exchange capacity, chemical and osmotic stability, sufficient mechanical strength and elasticity, high rate of ion-exchange and sorption processes, high permeability of filtrating layers. Support free fibrous cerium(IV) phosphate sheets have been used for the chromatographic separation of inorganic ions [136] and have been found selective towards Pb(II), Ag(I) and Co(II). Recently, a possibility has also been explored to develop some organic-inorganic ion-exchangers [137]. Their inorganic matrix has a structure similar to that of the layers of $\alpha$-Zr $(HPO_4)_2$. $H_2O$.

Synthetic inorganic ion-exchangers have found applications in various fields [49]. Purification of coolant water in closed cycle reactor systems [138-140], chemical separation of radioactive ions [141] and extraction of uranium from sea water using titanium oxide [142] are some of the examples to illustrate their use in nuclear field. Zirconium phosphate has also been used in portable renal dialysis systems [143], because of its high selectivity for $NH_4^+$ ions. Production of spherical particles [144, 145], precipitation of

silica gel onto the zirconium phosphate particle [146] and production of zirconium phosphate in a polytetrafluoroethylene (flouroplast) coating [147] are some of the attempts to improve the stability of zirconium phosphate. Inorganic ion-exchangers are also important in the field of water softening, as they are, generally, highly selective for common metal ions. Zirconium phosphate has been reported as a reagent used in detergents [148]. Its application in chromatography has been demonstrated by a gas chromatographic separation of anions [149]. Similarly, chlorohydrocarbons and mercaptans have been effectively separated on crystalline potassium zirconium phosphate [150]. Use as catalysts is another interesting feature of inorganic ion-exchangers. Since they are solid acids they may have potential application in titrations [151, 152]. Alcohol dehydration [153, 154] and one step synthesis process of methyl isobutylketone [155, 156] can also be mentioned in this context. In addition to this a number of catalyzed oxidations have been reported such as butane to maleic acid [157], CO to $CO_2$ [158] and oxidative wastewater treatment [159]. Inorganic membranes are attractive from the standpoint of their stability towards acids, temperature and high radiation fields. They would permit a higher temperature to be used and higher efficiencies to be attained as compared to the organic resins [160]. In the field of corrosion also, inorganic ion-exchangers have found applications. Labody and Ronay [162] have shown that the corrosion was lower on a steel tube wrapped with a thin sheet of a hydrous oxide as compared to the one without the sheet. Adsorption behaviour of inorganic ion-exchangers for pesticides is an important aspect of study which has so far been lacking. The adsorption of pesticides on soils is affected by the presence of metal ions in soils as they have an important role in modifying its nutritional status. Inorganic materials possessing ion-exchange properties are known to be selective for various metal ions and hence their presence in soil may have some far reaching consequences for its more judicious use in field crops. An attempt

has been made in this direction by studying the adsorption of carbofuran on antimony (V) silicate [162]. This study has indicated a highly enhanced adsorption of carbofuran on antimony (V) silicate as compared to soil. It may be true for other materials of this class too. Thus, inorganic ion-exchangers have multiphase applications. They can also be utilized as impregnants on papers and glass plates in planar chromatography. Further, they can be used as ion-selective electrodes and as packing materials in ion-chromatography in the environmental analysis.

The main use of inorganic ion-exchangers is in the nuclear energy industry for the separation of selected nucleides from the wastes of reactor fuels, as they are superior in resistance to radiation and temperature increase as compared to their organic counterparts. The additional qualities which any ion-exchange material must possess in order to obtain wide applications may be summarized as follows:

1. The material must be virtually insoluble in strongly acid or alkaline solutions as such media are often encountered in reprocessing work.
2. Its exchange capacity must be high enough to ensure a practical operation.
3. Its sorption and elution behaviour must be rapid so that column can be operated at reasonable flow rates.
4. Its resistance to attrition must be good so that columns can be loaded and eluted many times without severe clogging or channelling.
5. The ion-exchanger must be of a reproducible behaviour so that a minor change in the method or material used for preparation does not cause major changes in its performance.
6. Its selectivity for some metal ions must be high, so that, a convenient separation between different ions, or at least types of ions, can be affected by suitable variation.

7. If a separation is pH dependent then the ions to be sorbed are able to compete successfully with the hydrogen ions for the functional groups within the available range of pH.

It follows from the number and purposes of the published works on the use of inorganic ion-exchange materials in analytical chemistry that their main application lies in their use for the selective separation and concentration of elements in various mixtures. They are and will be used intensively in combination with neutron activation analysis of biological and very pure materials. It is also clear from the above that inorganic ion-exchangers are still the flourishing materials possessing a potential of showing many novel applications. The protection of the environment and health protection require strict limits on the concentrations of the heavy metals and radioisotopes in the hydrosphere. The analyst must often determine the studied element that is highly diluted in a large volume of water or air. It is often necessary to treat a large amount of sea or river water or complex industrial effluents with high salt contents. The use of suitable inorganic ion-exchange materials with high selectivity for the studied elements often facilitates their concentration and separation, which are necessary for successful determination. It is thus necessary to employ materials with suitable sorption properties, high selectivity, and high chemical and mechanical stability. Inorganic ion-exchange materials can be especially useful in this field.

In view of the above our aim has been to develop a hybrid material which may possess a high stability both chemical and thermal and may show an excellent reproducibility in its ion-exchange behaviour. As a result acrylamide-zirconium phosphate has been prepared which has shown promising ion-exchange characteristics. It has proved to be highly selective for mercury.

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# Chapter 2

# Synthesis and Ion-Exchange Behaviour of Acrylamide Zirconium(IV) Phosphate Hybrid Inorganic Ion-Exchanger

## INTRODUCTION

The organic ion exchangers are well known for their uniformity, chemical stability and for the easy control over their ion-exchange properties through synthetic methods. Inorganic ion-exchangers have established their place in Analytical Chemistry due to their resistance to heat and radiation and their differential selectivity for metal ions. In order to get a combination of these advantages and to increase the interlayer distance of layered inorganic ion-exchangers so that large species or complexes could be exchanged, many hybrid type exchangers have been developed by incorporation of a polymeric material into inorganic matrix, by way of pillaring or by other non-pillaring methods [1-5].

Zirconium based ion-exchangers have received attention because of their excellent ion-exchange behaviour and some important chemical applications in the field of ion-exchange, ion-exchange membranes, solid state electrochemistry and phase transition etc. They possess good stability towards temperature, ionizing radiations and oxidizing solutions.

The present study is an extension of our earlier studies [6-7] in this direction on the materials based on zirconium. An acrylamide based zirconium phosphate has been synthesized and characterized which has shown a promising behaviour as ion-exchanger. The following pages summarize our such a study.

## 2.1 EXPERIMENTAL

### 2.1.1 Reagents and Chemicals:

Zirconyl oxy chloride ($ZrOCl_2.8H_2O$) and acrylamide ($CH_2CHCONH_2$) were the CDH (India) products while ortho phosphoric acid ($H_3PO_4$) was a Qualigens (India) product. All other reagents and chemicals were of AnalaR grade.

### 2.1.2 Instrumentation:

Spectrophotometric determinations were carried out on an Elico SL 171 Spectrophotometer, while X-ray diffraction studies were performed on a Philips Analytical X-ray B.V. diffractometer type PW 1710. pH measurements were performed using an Elico Model LI-10 pH meter and IR studies were carried out by the KBr disc method. For thermogravimetric analysis a Cahn thermobalance Model 2050 was used.

### 2.1.3 Preparation of the reagent solutions:

Solutions of Zirconyl oxy chloride, acrylamide, phosphoric acid, and hydrogen peroxide were prepared in demineralized water (DMW).

### 2.1.4 Synthesis of the ion-exchange material:

A number of samples were prepared by adding 0.05M Zirconyl Oxy chloride, 0.1M acrylamide, 2M ortho phosphoric acid and 0.5% $H_2O_2$. The pH of the resulting gel was maintained 0-1 by adding concentrated $HNO_3$ with constant stirring. The resulting slurry obtained under these conditions was stirred for 2 hrs at a temperature of 70 ± 5°C, using a magnetic stirrer. The resulting slurry obtained was then filtered, and washed with demineralized water (pH ~ 6). The material was finally dried as usual at 45°C. The dried gel was then cracked into small granules by putting in DMW and converted into the $H^+$- form by treating with 1M $HNO_3$ for 24 hrs with occasional shaking and intermittently replacing the supernatant liquid with fresh acid. The material thus obtained was then washed with demineralized water to remove the excess acid before drying finally at 45°C, and sieved to obtain particles of size 50-70 mesh. Table

2.1 and 2.2 gives the experimental details of the synthesis of the various samples of the material. Thus, on the basis of its ion exchange capacity sample 1 of Table 2.2 is selected for further studies.

## 2.2 CHEMICAL AND PHYSICO-CHEMICAL STUDIES

### 2.2.1 Ion-Exchange Capacity (i.e.c.):

This was determined by the usual column process taking 1 gram of the material ($H^+$- form) in a glass tube of internal diameter of ~ 1 cm, fitted with glass wool at its bottom. 250 ml of 1M $NaNO_3$ solution was used as eluant, maintaining a very slow flow rate (~ 0.5ml $min^{-1}$). The effluent was titrated against a standard alkali solution to determine the total $H^+$ - ions released. Table 2.3 summarizes the ion exchange capacity of the material for various metal ions.

### 2.2.2 Effect of Eluant Concentration on the Ion-Exchange Capacity:

The extent of elution was found to depend upon the concentration of the eluant. Hence a fixed volume (250ml) of the $NaNO_3$ solution ofvarying concentrations was passed through the column containing 1gm of the exchanger and the effluent was titrated against a standard alkali solution for the $H^+$- ions eluted out. Fig. 2.1 shows the variation of the $H^+$- ions eluted out with the different concentrations of the eluant. The optimum concentration of the eluant for a complete elution of $H^+$- ions in 250 ml $NaNO_3$ solution was found to be 1M.

### 2.2.3 Elution Behaviour:

The column containing 1g in the $H^+$- form was eluted with 1M $NaNO_3$ solution in different 10ml fractions having a standard flow rate of 0.5ml $min^{-1}$ and 10ml fractions of the effluent were collected. They were titrated for the $H^+$- ions released against a standard NaOH solution. This experiment was conducted to find out the minimum volume necessary for a complete elution of $H^+$- ions, which reflects the efficiency of the column. The result is shown in Fig. 2.2.

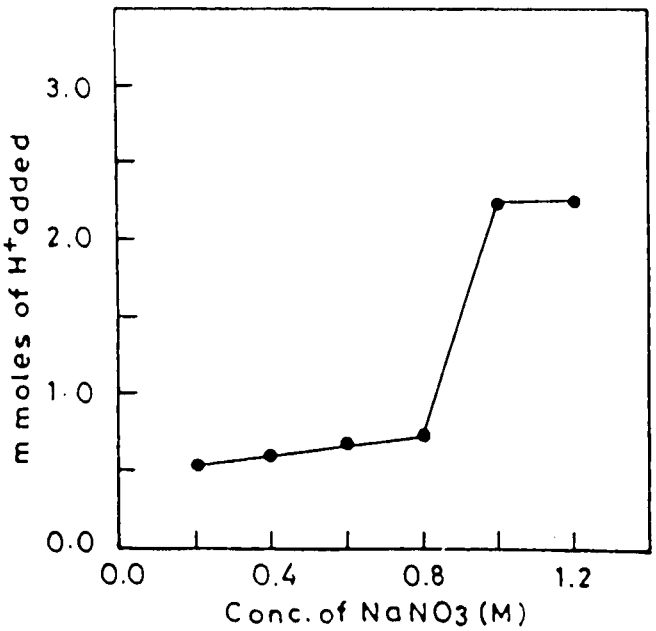


Fig. 2.1 Concentration plot of acrylamide zirconium (IV) phosphate.

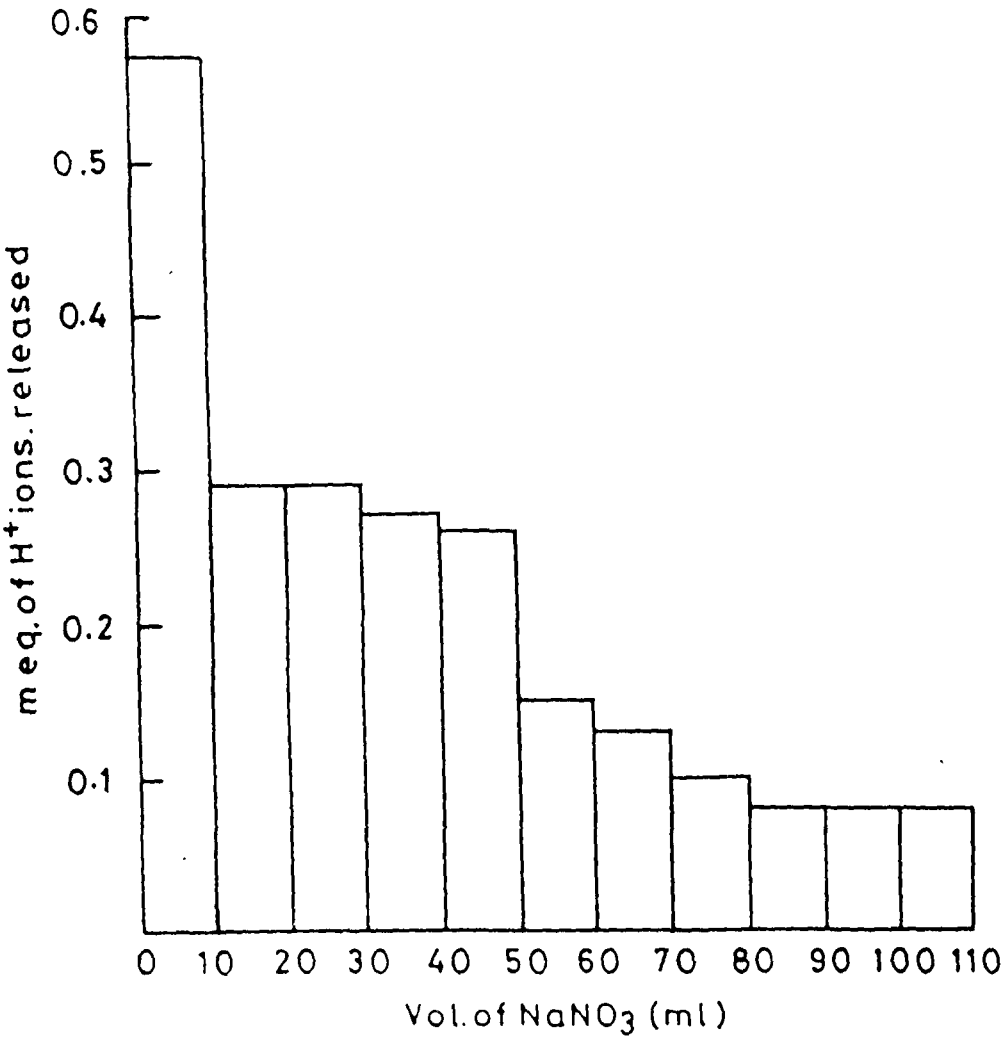


Fig. 2.2 Histograms showing the elution behaviour of acrylamide zirconium (IV) phosphate.

**Table 2.1** Synthesis of various samples of acrylamide based zirconium (IV) phosphate.

| S.No. | Conc. of Zr. Solution | Conc. of $H_3PO_4$ | Conc. of acrylamide | Ion Exchange capacity (meq dry $g^{-1}$) |
|---|---|---|---|---|
| 1 | 0.1M | 2 M | 0.05M | 0.85 |
| 2 | 0.1M | 1 M | 0.5M | 0.8 |
| 3 | 0.1M | 1 M | 0.1M | 1.4 |
| 4 | 0.5M | 2 M | 0.5M | 1.4 |
| 5 | 0.05M | 2 M | 0.1M | 2.0 |

**Table 2.2** Synthesis of acrylamide based zirconium (IV) phosphate by varying the conc. of $H_2O_2$.

| S.No. | Conc. of Zr solution | Conc. of $H_3PO_4$ | Conc. of acrylamide | Conc. of $H_2O_2$ (%) | Heating time (Hrs) | Ion-exchange capacity (meq dry $g^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0.05M | 2M | 0.1M | 0.5 | 2 | 2.26 |
| 2 | 0.05M | 2M | 0.1M | 1 | 2 | 0.25 |
| 3 | 0.05M | 2M | 0.1M | 2 | 2 | 0.3 |
| 4 | 0.05M | 2M | 0.1M | 3 | 2 | 0.6 |
| 5 | 0.05M | 2M | 0.1M | 4 | 2 | 0.84 |
| 6 | 0.05M | 2M | 0.1M | 0.5 | 4 | 0.44 |

### 2.2.4 Thermal Studies:

1gm samples of the material were heated at various temperatures for 1 hr each in a muffle furnace and their ion-exchange capacity was determined by the column process after cooling to room temperature. The results are summarized in Table 2.4, Fig. 2.3 shows the TGA curve of the material.

### 2.2.5 pH Titrations:

pH titrations were performed by the batch process using the method of Topp and Pepper [8]. 500 mg portions of the exchanger in the $H^+$- form were placed in each of the several 250 ml conical flasks followed by the equimolar solution of alkali metal chlorides and their hydroxides in different volume ratios, the final volume being 50 ml to maintain the ionic strength constant. The pH of the solution was recorded after equilibrium and was plotted against the milliequivalents of the $OH^-$ ions added. The results are shown in Fig. 2.4.

### 2.2.6 IR Studies:

IR studies were carried out by the KBr disc method. Fig. 2.5 shows the IR spectrum of the material.

### 2.2.7 X-Ray Studies:

X-ray diffraction studies were performed on a Philips Analytical X-ray B.V. diffractometer type PW 1710. Fig. 2.6 shows the X-ray diffraction pattern of the material. Table 2.5 summarizes the results of these studies.

### 2.2.8 Distribution Studies:

200 mg portions of the exchanger in $H^+$- form were taken in 20ml of the different metal ion solutions in the required medium and kept for 24 hrs with intermittent shaking to attain equilibrium. The initial metal ion concentration (0.001M) in the solution was so adjusted that it did not exceed 3% of total ion-exchange capacity of the material. The determinations before and after equilibrium were carried out volumetrically using EDTA [9] as the titrant.

**Table 2.3** Ion-Exchange capacity of acrylamide based zirconium (IV) phosphate for various metal solutions.

| **Metal solution** | **Ion-exchange capacity (meq dry $g^{-1}$)** |
|---|---|
| $LiNO_3$ | 0.2 |
| $NaNO_3$ | 2.26 |
| $KNO_3$ | 1.3 |
| $Mg(NO_3)_2$ | 1.38 |
| $Ca(NO_3)_2$ | 2.58 |
| $Sr(NO_3)_2$ | 3.28 |
| $BaCl_2.2H_2O$ | 1.5 |

**Table 2.4** Thermal stability of acrylamide based zirconium (IV) phosphate after heating to various temperatures for 1 hour.

| **Drying temperature(°C)** | **Na+ ion-exchange Capacity (meq dry $g^{-1}$)** | **Change in colour** | **% Retention of i.e.c.** |
|---|---|---|---|
| 45 | 2.26 | White | 100 |
| 100 | 2.26 | White | 100 |
| 200 | 2.26 | White | 100 |
| 400 | 0.18 | Dirty white | 9 |

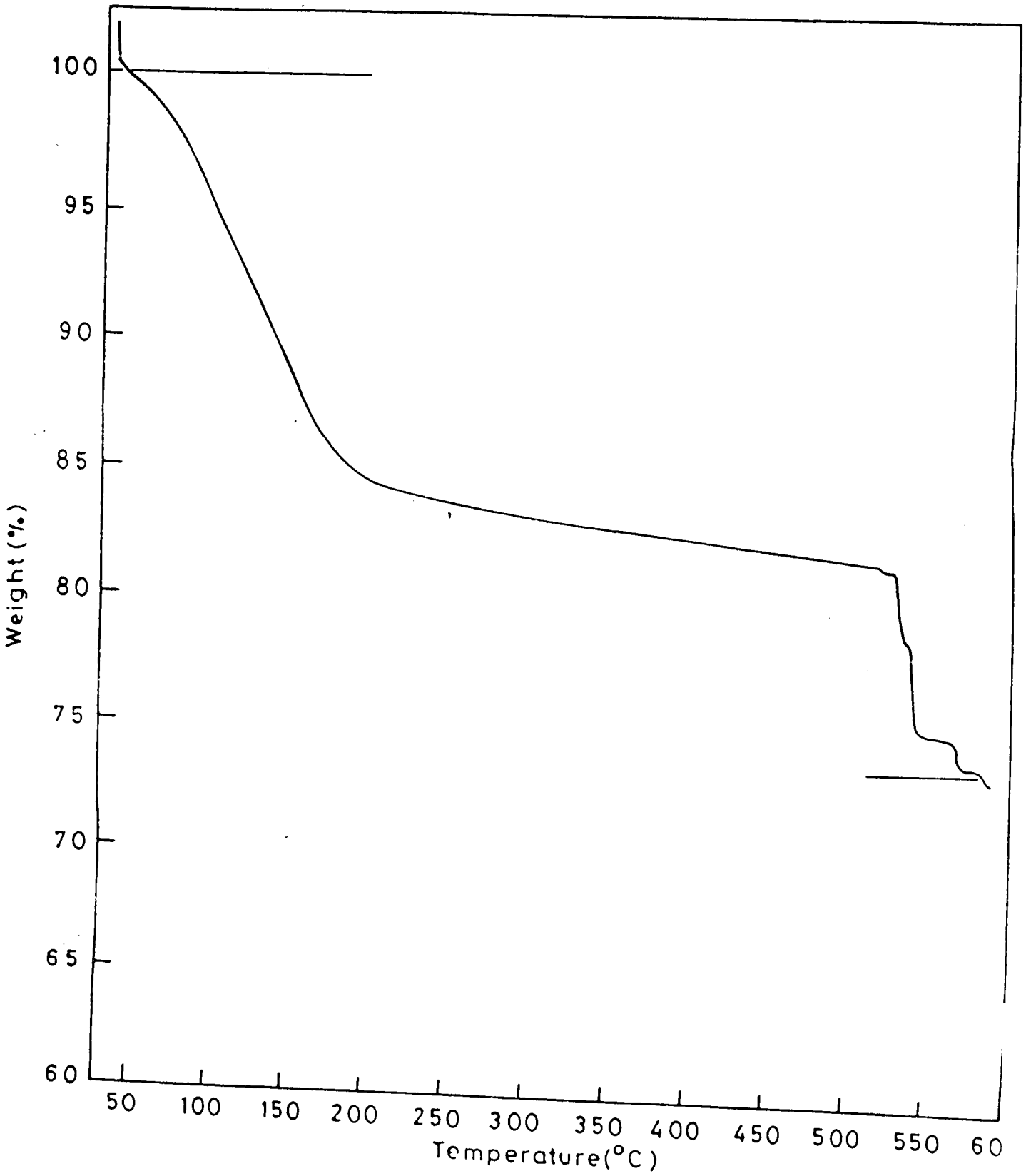


Fig. 2.3 Thermogravimetric (TGA) curve of acrylamide zirconium (IV) phosphate.

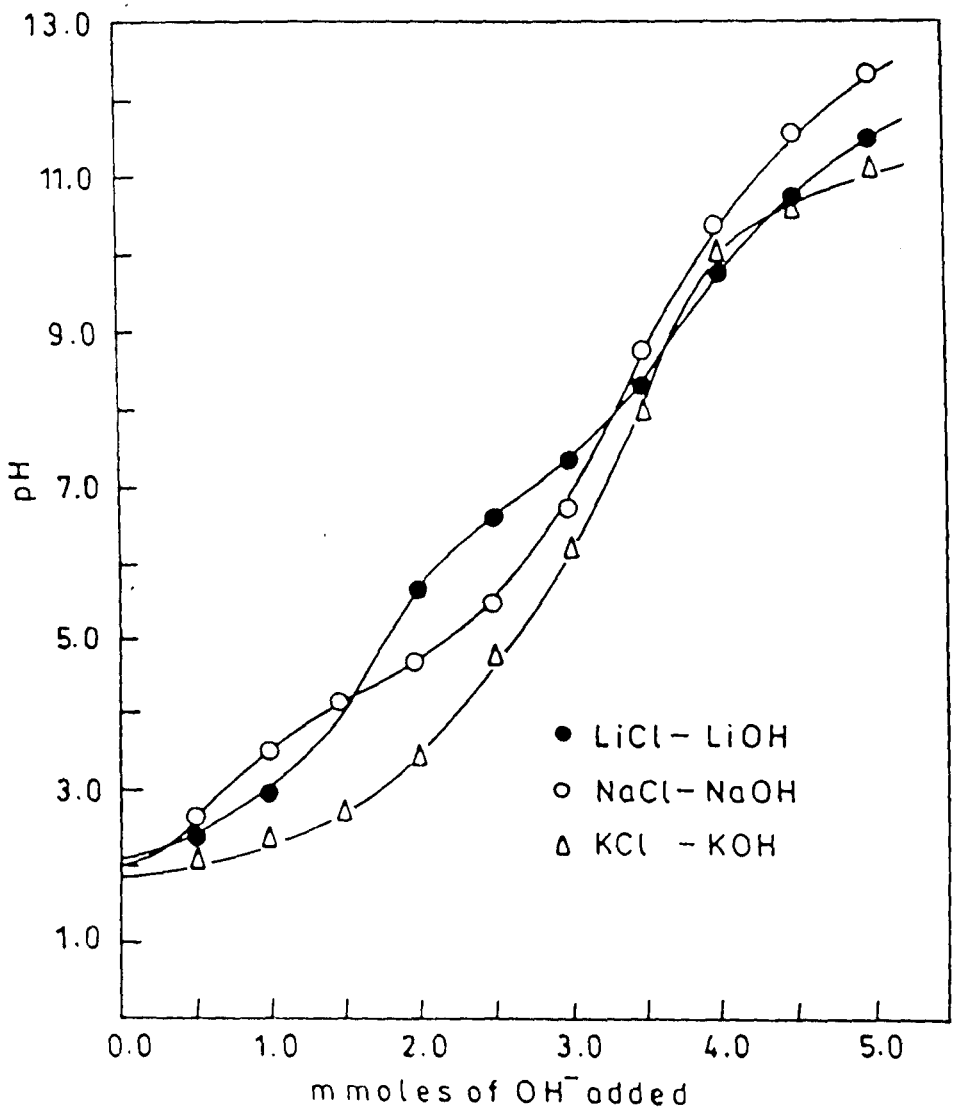


Fig. 2.4 Equilibrium pH titration curve of acrylamide zirconium (IV) phosphate.

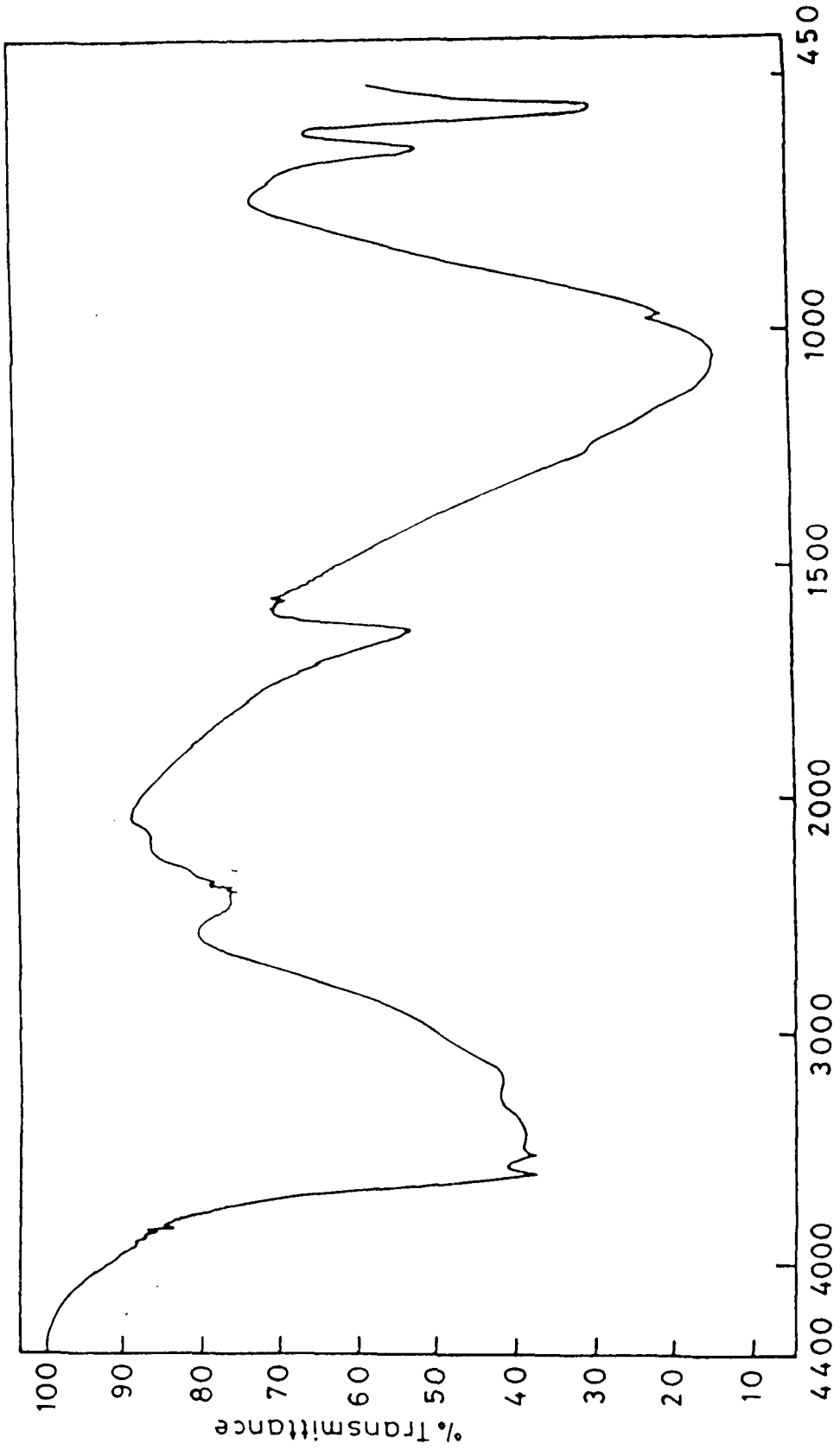


Fig. 2.5 IR spectrum of acrylamide zirconium (IV) phosphate.

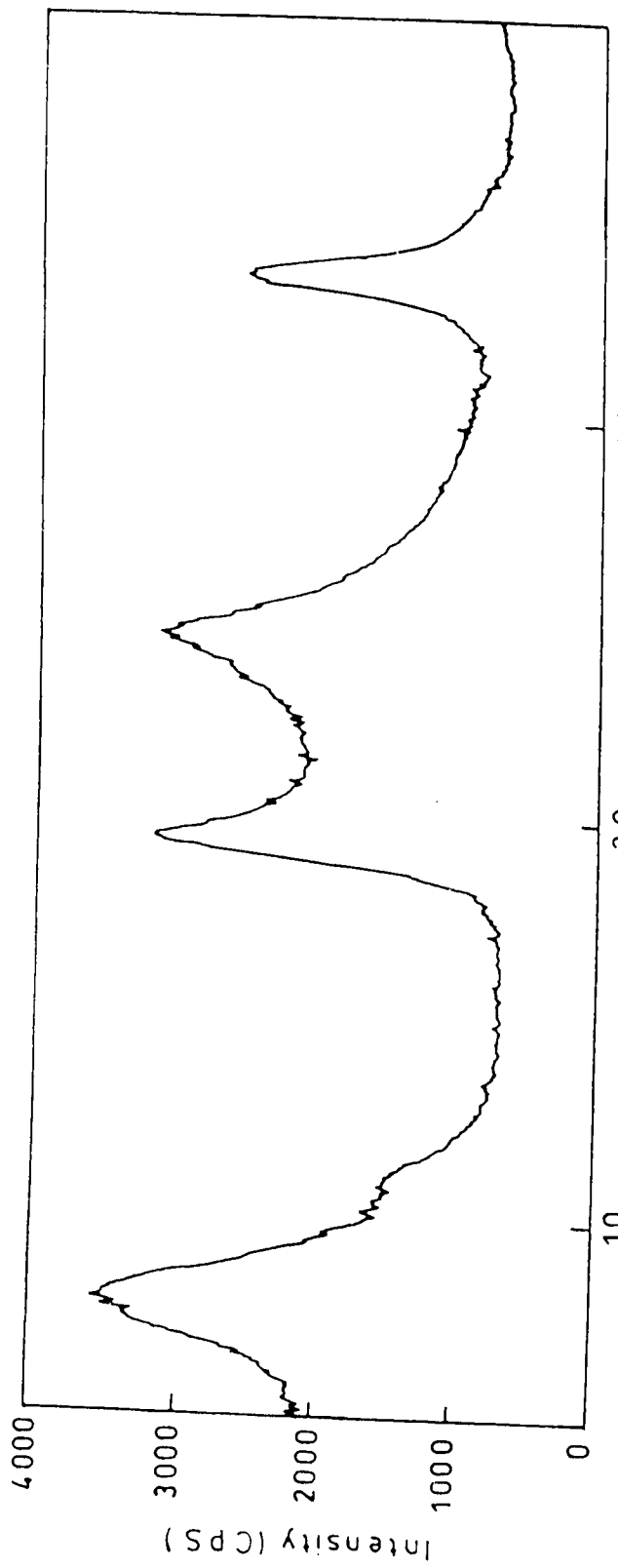


Fig. 2.6 X-ray diffraction pattern of acrylamide zirconium (IV) phosphate.

The $K_d$ values, as summarized in Table 2.6 were obtained by the formula:

$$K_d = \frac{I-F}{F} \times \frac{V\,(ml)}{M\,(gm)}$$

I = Initial metal ion concentration

F = Final metal ion concentration

V = volume of the solution

M = mass of the exchanger

**2.2.9 Separations Achieved:**

Several binary separations were tried using a column of internal diameter ~ 0.6 cm containing 2 gm of the material. The column was washed thoroughly with demineralized water and the mixture to be separated was loaded on it, maintaining a flow rate of ~ 2-3 drops $min^{-1}$ (0.15 ml $min^{-1}$). The separation was achieved by passing a suitable solvent through the column as eluant and the metal ions in the effluent were determined quantitatively by EDTA titrations. Table 2.7 and Fig. 2.7 give the salient features of the separations.

**Table 2.5** X-ray diffraction data of acrylamide based zirconium (IV) phosphate

| Peak No. | Angle (2θ°) | FWHM | d-value | Intensity | I/I$_0$ |
|---|---|---|---|---|---|
| 1 | 7.940 | 0.141 | 11.1257 | 3569 | 100 |
| 2 | 19.520 | **** | 4.5439 | 3203 | 90 |
| 3 | 24.640 | 0.165 | 3.6100 | 3149 | 88 |
| 4 | 33.440 | 0.118 | 2.6774 | 2427 | 68 |

**Table 2.6** $K_d$ values of metal ions on acrylamide based zirconium (IV) phosphate in DMW, hydrochloric acid, nitric acid and perchloric acid media.

| Metal ions | DMW | HCl | | | $HNO_3$ | | | $HClO_4$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.01M | 0.1M | 1M | 0.01M | 0.1M | 1M | 0.01M | 0.1M | 1M |
| Mg(II) | 1484.6 | 610.3 | 564.5 | 564.5 | 1616.6 | 692.3 | 635.7 | 795.6 | 635.7 | 488.5 |
| Ca(II) | 614.2 | 589.6 | 471.4 | 440.5 | 1566.6 | 952.6 | 809 | 733.3 | 506 | 455.5 |
| Sr(II) | 1850 | 408.6 | 333.3 | 244.1 | 619.4 | 265.6 | 225 | 963.6 | 515.7 | 387.5 |
| Ba(II) | 3333.3 | 1187.5 | 1111.7 | 1111.7 | 1616.6 | 1484.6 | 1484.6 | 1772.7 | 1273.3 | 880.9 |
| Cd(II) | 6400 | 747.8 | 712.5 | 680 | 875 | 596.4 | 509.3 | 828.5 | 712.5 | 596.4 |
| Pb(II) | 2800 | 2220 | 1446.6 | 728.5 | 1188.8 | 759.2 | 673.3 | 1446.6 | 1350 | 1121.0 |
| Mn(II) | 2566.6 | 1233.3 | 1100 | 548.6 | 1163.1 | 674.1 | 485.3 | 860 | 531.5 | 380 |
| Cr(II) | 50 | 15.38 | 15.38 | 15.38 | 7.14 | 7.14 | 7.14 | 7.14 | 7.14 | 7.14 |
| Co(II) | 1366.6 | 1366.6 | 1194.1 | 856.5 | 4300 | 2650 | 1275 | 3042.8 | 1733.3 | 1366.6 |
| Cu(II) | 5750 | 2825 | 1200 | 836 | 3800 | 1362.5 | 1131.5 | 4580 | 2027.2 | 1070 |
| Hg(II) | 11250 | 11250 | 11250 | 7466.6 | 22600 | 4440 | 3683.3 | 11250 | 4440 | 3683.3 |
| Ni(II) | 3371.4 | 3371.4 | 1329.4 | 1250 | 1635.7 | 1520 | 1418.75 | 4760 | 2600 | 2109 |

**Table 2.7** Binary separations of metal ions achieved on acrylamide based zirconium (IV) phosphate columns.

| S.No | Separation achieved | | Amount loaded (μg) | | Amount found (μg) | | Error (%) | | Eluant used | Volume of eluant (ml) |
|---|---|---|---|---|---|---|---|---|---|---|
| | $M_1$ | $M_2$ | $M_1$ | $M_2$ | $M_1$ | $M_2$ | $M_1$ | $M_2$ | | |
| 1 | Ni(II) – Hg(II) | | 4579.94 | 5504.56 | 4470.89 | 5504.56 | -2.38 | 0 | Ni:0.1M HCl | 70 |
| | | | | | | | | | Hg: 1M HCl + 1M $NH_4Cl$ | 70 |
| 2 | Cd(II) – Hg(II) | | 4858.40 | 5504.56 | 4742.72 | 5504.56 | -2.38 | 0 | Cd: 1M $HNO_3$ | 60 |
| | | | | | | | | | Hg: 1M HCl + 1M $NH_4Cl$ | 70 |
| 3 | Pb(II) – Hg(II) | | 4968.15 | 5504.56 | 4968.15 | 5379.46 | 0 | -2.27 | Pb: 1M HCl | 50 |
| | | | | | | | | | Hg:1M HCl + 1M $NH_4Cl$ | 70 |
| 4 | Mg(II) – Hg(II) | | 4038.45 | 5504.56 | 4134.611 | 5379.46 | +2.38 | -2.27 | Mg: 0.1M HCl | 70 |
| | | | | | | | | | Hg: 1M HCl + 1M $NH_4Cl$ | 80 |

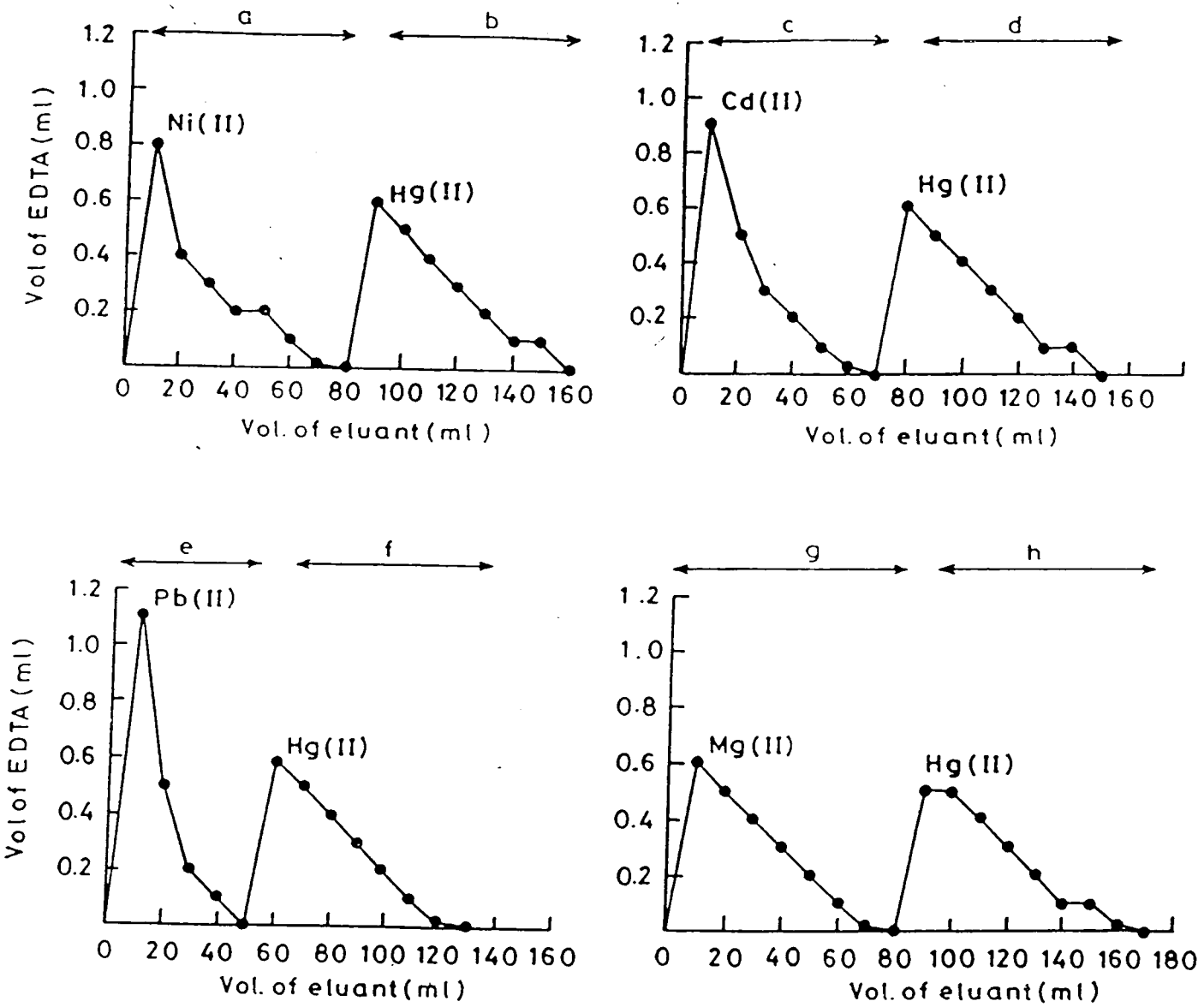


Fig.2.7 Separation of Ni(II) from Hg(II); Cd(II) from Hg(II); Pb(II) from Hg(II); and Mg(II) from Hg(II) on acrylamide zirconium(IV) phosphate columns: (a,g) 0.1M HCl; (b,d,f,h) 1M HCl + 1M $NH_4Cl$; (e) 1M HCl; (c) 1M $HNO_3$.

## RESULTS AND DISCUSSION

A comparison reveals that acrylamide based zirconium phosphate prepared during these studies possess a better ion-exchange capacity (2.26 meq dry gram$^{-1}$) than the materials prepared earlier [10,11]. Another most peculiar characteristic of this material is its thermal stability. The material retains 100% of its ion-exchange capacity on heating upto 200°C.

The elution behaviour indicates that the exchange is quite fast and almost all the $H^+$- ions are eluted out in the first 110 ml of the effluent from a column of 1 gm exchanger (Fig. 2.2). The optimum concentration of the eluant was found to be 1M (Fig. 2.1) for a complete removal of $H^+$-ions from the above column. Moreover, the pH titration studies (Fig. 2.4) reveal that the material behaves as a bifunctional acid for $Li^+$- ions showing its theoretical ion-exchange capacity at equilibrium ~ 3.5 meq gm$^{-1}$. The bifunctional behaviour becomes less prominent in case of the $H^+$ - $Na^+$ exchange. The ion-exchange capacity for this ion is found to be little less (~ 3.25 meq gm$^{-1}$). However, in case of $K^+$ the exchanger appears to be a monofunctional acid i.e., the exchange process is completed in a single step. The value of the ion-exchange capacity further decreases in this case (~ 3 meq gm$^{-1}$). This discrepancy may be explained on the basis of the hydrated radii of these ions, which are in the order $Li^+ > Na^+ > K^+$. A metal ion with a lower hydrated radii may be exchanged more effectively on the exchanger surface.

The TGA curve (Fig. 2.3) shows a 16% weight loss up to ~ 200°C, which may be due to the removal of the external water molecules "n" from the material [12]. The slow weight loss between 200°C and 510°C may be due to the decomposition of the organic part of the material. An abrupt loss of weight between 510°C and 590°C may be ascribed to the condensation of $H_3PO_4$ to $P_2O_7$ groups [13]. At 590°C onwards the smooth horizontal curve represents the formation of the pyrophosphate phase.

The number of external water molecules (n) is calculated using the Alberti's equation [14] and with the help of composition of the material which is a separate study under progress.

The IR studies (Fig. 2.5) confirm the presence of the external water molecules in addition to the O-H groups and the metal oxide present in the material. The metal oxide bands are observed at 610 $cm^{-1}$, while bands at 508$cm^{-1}$ and 1050 $cm^{-1}$ indicates the presence of $PO_4^{3-}$ group. The presence of external water molecule is indicated by the band at 1600 $cm^{-1}$, in addition to its usual range at 3000-3500$cm^{-1}$. The peak at 1380 $cm^{-1}$ may be ascribed to the presence of $-NH_2$ groups in the acrylamide moietie [15].

The X-ray diffraction pattern (Fig. 2.6) of the material exhibits very sharp and well defined peaks indicating a well crystalline character of the material.

The distribution behaviour of the metal ions (Table 2.6) shows a high selectivity of the material for Hg(II) ions, indicating its importance in environmental studies. It was demonstrated by practically achieving some binary separations involving Hg(II), for example: Hg(II)-Ni(II), Hg(II)-Cd(II), Hg(II)-Pb(II), and Hg(II)-Mg(II), as summarized in Table 2.7. The results were found to be quite precise and reproducible.

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